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Electron-impact excitation of [1.1.1] propellane

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Electron-impact excitation has been developed into a powerful tool for the study of the excited states and temporary anions (resonances) of polyatomic molecules.[1,2] Such studies have, for example, provided a great deal of information about the excited states and resonances of small hydrocarbons,[2,3] information that is, in turn, useful in understanding aspects of bonding, reactivity, and photochemistry. However, theoretical contributions to the study of electron-impact excitation in larger molecules have mostly been confined to predictions of the energies of excited states, using conventional bound-state quantum chemistry, and of the energies and widths of resonances, e.g., by the stabilization method.[4] With recent advances in the capabilities of high-performance parallel computers[5] and with the development of methods for electron–molecule scattering that exploit them,[6–8] it is now possible to contemplate detailed *ab initio* studies of the cross sections for fairly large polyatomic systems. Such studies will complement experiments both as an independent source of scattering data and as aids in the analysis and assignment of significant experimental features.

We have calculated cross sections for low-energy electron-impact excitation of the C_5H_6 molecule [1.1.1] propellane (Fig. 1), motivated by the recent experimental studies of Schafer *et al.*[9] Here we report differential and integral cross sections for excitation of the $(5a_1' \rightarrow 3a_2'')\ ^3A_2''$ state, which is the lowest-lying excited-state of this molecule. Of particular interest in the experimental cross section is a pronounced low-energy peak that has been assigned as a $(5a_1')(3a_2'')^2$ core-excited shape resonance.[9] Our results support this assignment and provide new information about both the magnitude of the cross section and the details of the angular distribution.

In these calculations, we have used our implementation of the Schwinger multichannel (SMC) method[10] for distributed-memory parallel computers.[6–8] The two principal steps in calculations of this type are construction of two-electron integrals involving three Cartesian Gaussians and a plane wave, and transformation of those integrals to matrix elements between Slater determinants that appear in the SMC expression.[10] The current version of our SMC program has been somewhat optimized for the Intel Touchstone DELTA machine[5] and achieved sustained performance of 950 000 (contracted) integrals/s for the first of these steps, and of 4 GFLOP (4×10^9 floating-point operations/s) in the transformation step, in the course of these propellane calculations. We expect this performance to increase considerably with further optimization and larger problem sizes.

The Gaussian basis set used in the present work for description of both target and scattering wave functions was constructed from the 4*s*3*p* C basis and 3*s* H basis of Dunning,[11] supplemented by one *s* (exponent 0.0473) and one *d* function (exponent 0.8) on C and one *p* function (exponent 1.0) on H, for a total of 136 contracted and 197 primitive Gaussians. We judged this basis sufficient since it and a smaller basis gave nearly identical results in calculations of elastic scattering cross sections, which will be reported elsewhere.[12] All calculations were done in the ground-state D_{3h} geometry optimized at the SCF level using the 6-31G^{**} basis set.[13] We obtained an SCF ground state energy of -192.730470 a.u. Using the IVO procedure,[14] we calculated a $(5a_1' \rightarrow 3a_2'')^3\ A_2''$ vertical excitation threshold of 4.743 eV, which compares well with experimental value, 4.70 eV.[9]

The $(5a_1' \rightarrow 3a_2'')\ ^3A_2''$ threshold is considerably lower than that of any other excited state, and in particular much lower than the threshold (7.26 eV) of the first valence singlet excitation.[9] We therefore expect that a two-channel approximation, including only the ground and $^3A_2''$ states, should be reliable, and have used it here.

In Fig. 2 we show the calculated cross section for excitation of the $(5a_1' \rightarrow 3a_2'')\ ^3A_2''$ transition, together with the contribution from the totally symmetric $^2A_1'$ symmetry of the electron-molecule system. A narrow feature attributable to the A_1'' representation is clearly visible. This overall symmetry implies an a_2'' symmetry for the scattered electron and therefore supports an interpretation of the peak as arising from a $(5a_1')(3a_2'')^2$ core-excited shape resonance, as proposed by Schafer *et al.*[9] The shift between the exper-

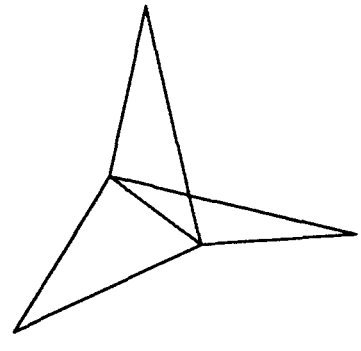

FIG. 1. [1.1.1] Propellane.

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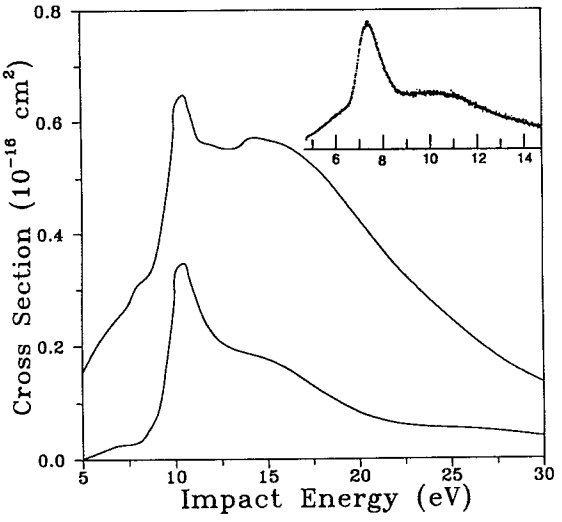

FIG. 2. Electron-impact excitation cross section for the $(5a_1' \rightarrow 3a_2'')$ $^3A_2''$ state of [1.1.1] propellane (upper curve), and its $^2A_1'$ symmetry component (lower curve). Inset: experiment of Ref. 9.

imentally observed resonance position, about 2.7 eV above threshold, and the calculated position, about 5.7 eV above threshold, is typical for calculations in which target polarization is neglected, and is comparable to the shift seen in the position of the elastic-channel shape resonance.[9,12]

Figure 3 shows our calculated differential cross section at 10.5 eV impact energy. The differential cross section, which is fairly isotropic near threshold, becomes strongly backward peaked in the vicinity of the resonance. At 10.5 eV, the composition of the differential cross section in terms of Legendre polynomials $P_K(\cos\theta)$ is dominated by P_3, consistent with partial waves $\ell=0$ (or 2) in the entrance channel and $\ell=3$ in the exit channel, as would be expected for low-energy scattering via the $3a_2''$ resonance.

As pointed out elsewhere,[9,15–17] [1.1.1] propellane is a remarkable molecule, formally a saturated hydrocarbon but with considerable orbital rehybridization arising from the large ring strain. The low-energy valence triplet state and the low-energy shape resonance in the elastic channel, for instance, are characteristic of alkenes. Similar though less marked effects of ring strain on resonances are observed in cyclopropane and other small ring systems.[18,19] However, the core-excited $(5a_1')(3a_2'')^2$ resonance appears to be especially unusual. The somewhat analogous $(\pi^*)^2$ resonance in ethylene is not seen in recent calculations,[20,21] in spite of limited experimental evidence for its existence.[22] The greater spatial extent of the $3a_2''$ orbital compared to the π^* orbital of ethylene may facilitate the temporary accommodation of the electrons that gives rise to the resonance. An alternative mechanism is more effective trapping by the angular momentum barrier: The $3a_2''$ orbital is largely $\ell=3$, whereas the ethylene π^* orbital is largely $\ell=2$.

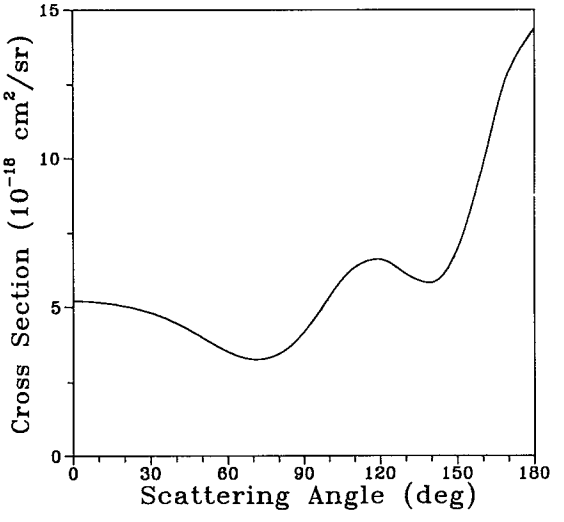

FIG. 3. Differential cross section for electron-impact excitation of the $(5a_1' \rightarrow 3a_2'')$ $^3A_2''$ transition at 10.5 eV (on resonance).

In summary, we have calculated *ab initio* cross sections for excitation of the $(5a_1' \rightarrow 3a_2'')$ $^3A_2''$ state by low-energy electron impact, observing a core-excited temporary anion of $^2A_1'$ symmetry and probable configuration $(5a_1')(3a_2'')^2$. These results complement recent measurements[9] and confirm the resonance assignment. A more complete description of the calculations, including static-exchange results below the triplet threshold and differential cross sections for elastic and inelastic scattering, will be published separately.[12]

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